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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention]This invention relates to the manufacturing method of the polylactic acid fizz particles which have microbial degradability. It is related with the manufacturing method of the good polylactic acid fizz particles of the fizz which can obtain the foamed particle which is excellent in die shape reproducibility and foamed particle weld nature in detail.

[0002]

[Description of the Prior Art]The foamed particle Plastic solid which consists of resin, such as polystyrene, polyethylene, and polypropylene, is used broadly the shock absorbing material for a package, an agricultural production box, the fish box, the automobile member, the building material, the material of construction, etc. However, after use, since it is hardly decomposed by the microorganism when neglected under natural environment, these foamed particle Plastic solids have a possibility of causing the problem of environmental destruction by garbage dispersion. The microbially degradable resin etc. which research of the resin disassembled by the microorganism is also made on the other hand, and consist of polylactic acid as a suture for surgery until now, for example were put in practical use, and the old track record is stored. Lactic acid which is a raw material of polylactic acid makes corn etc. raw material, and it can manufacture now in large quantities and cheaply with bacterial coupling in recent years. Then, foam which consists of polylactic acid which has stored the track record in practicality, human body safety, and microbial degradability has been desired. As advanced technology about the foam which consists of polylactic acid, Patent Publication Heisei No. 508669 [five to], JP,4-304244,A, JP,5-139435,A, The thing about foamed particles, such as a thing about extrusion-foaming objects, such as JP,5-140361,A and JP,9-263651,A, JP,5-170965,A, JP,5-170966,A, and JP,2000-136261,A, is mentioned. In the advanced technology about the above-mentioned polylactic acid foam, the thing especially about a foamed particle can obtain the foam of

desired shape, without receiving geometrical restrictions comparatively, and since the physical-properties design according to the purposes, such as lightweight nature and buffer nature and adiathermancy, is also easy, it is promising especially as that practical. However, the foamed particle Plastic solid which consists of conventional polylactic acid welds particles mutually at the same time it is filled up with a fizz resin particle in a metallic mold and it makes this resin particle foam to it by a hot wind, and its weld nature of foamed particles is insufficient, and it is inferior to mechanical properties. In order to solve such a technical problem, to JP,2000-136261,A, adjusting the degree of crystallinity of a fizz resin particle to 0 to 20% is indicated, but. In the way the impregnating temperature of the volatilized type foaming agent of a statement adjusts a degree of crystallinity in this gazette, the fizz resin particle made into the purpose might be unable to be obtained.

[0003]

[Problem(s) to be Solved by the Invention]Then, this invention makes it the technical problem to provide the manufacturing method of the polylactic acid fizz particles excellent in die shape reproducibility and the fizz which can obtain the good foamed particle of foamed particle weld nature.

[0004]

[Means for Solving the Problem]In resin which uses polylactic acid as the main ingredients as a result of examining a manufacturing method of polylactic acid fizz particles wholeheartedly, in order that this invention persons may solve an aforementioned problem, When conditions with relation between the amount of being impregnated to a resin particle of this foaming agent and ambient temperature at the time of this being foaming agent impregnated are satisfied using carbon dioxide as a foaming agent, It finds out becoming the polylactic acid fizz particles excellent in die shape reproducibility and fizz which can obtain a good polylactic acid foamed particle of foamed particle weld nature, and came to complete this invention. That is, according to this invention, a method shown below is provided.

(1) A manufacturing method of polylactic acid fizz particles which uses polylactic acid as the main ingredients and with which calorific value in a differential scanning calorimetry is characterized by impregnating a resin particle of 15 or more J/g with carbon dioxide by ambient temperature [**] which satisfies a following formula (1).

[Equation 2]

$3 < \text{ambient temperature } [**] \leq -2.5X + 55$ (1)

[X show the amount of being impregnated of carbon dioxide to a resin particle (% of the weight) among a formula.]

(2) A manufacturing method of polylactic acid fizz particles given in the above (1) for which the amount of being impregnated of carbon dioxide to this resin particle is characterized by being 2.5 to 20 % of the weight.

[0005]

[Embodyment of the Invention]In this invention, the fizz particles (only henceforth fizz particles) which consist of resin which uses as the main ingredients the polylactic acid used as a molding material are manufactured by impregnating with carbon dioxide the resin particle produced from the base material resin which uses polylactic resin as the main ingredients as a foaming agent. The polylactic acid used as the main ingredients of said base material resin is converted into the weight of the monomer with which a polymerization is presented, and says the polymer which contains a lactic acid component 50% of the weight or more. In this thing, a copolymer with the aliphatic hydroxycarboxylic acid of the polymer of (1) lactic acid, (2) lactic acid, and others for example, (3) The mixture by the copolymer of lactic acid, aliphatic polyhydric alcohol, and aliphatic polycarboxylic acid, the copolymer of (4) lactic acid and other aliphatic polycarboxylic acid, and which combination of (5) aforementioned (1) - (4), etc. are included.

[0006]receiving polylactic acid in this invention -- an aliphatic series ester component -- at least 35-mol % -- the included biodegradable aliphatic polyester is mixable. A hydroxy acid polycondensation thing, the ring-opening-polymerization thing of lactone, the polycondensation thing of aliphatic polyhydric alcohol and aliphatic polycarboxylic acid, etc. are included by aliphatic polyester in this case. As a hydroxy acid polycondensation thing, they are mentioned by the polycondensation thing of hydroxybutyric acid, etc. and as a ring-opening-polymerization thing of lactone, Polycaprolactone etc. are mentioned and polybutylene succinate, a polybutylene succinate horse mackerel peat, poly (a butylene horse mackerel peat / terephthalate), etc. are mentioned as a polycondensation body of aliphatic polyhydric alcohol and aliphatic polycarboxylic acid. The mixing ratio of biodegradable aliphatic polyester to polylactic acid is 5 to 30 % of the weight preferably 50 or less % of the weight to both total quantity.

[0007]Use of the resin in which the melting point uses as the main ingredients 130-180 ** of polylactic acid which is 140-180 ** preferably in this invention is preferred.

[0008]The polymer which comprises L-lactide which is L-lactic acid, D-lactic acid, DL-lactic acid, or those annular dimers, D-lactide, DL-lactide, or those mixtures as an example of the polymer of the above-mentioned lactic acid can be mentioned.

[0009]As an example of the manufacturing method of polylactic acid, the mixture of lactic acid or lactic acid, and aliphatic hydroxycarboxylic acid is used as a raw material, for example, How to carry out dehydration polycondensation directly (for example, manufacturing method shown in U.S. Pat. No. 5,310,865), A ring-opening-polymerization method which polymerizes the cyclic dimer (lactide) of lactic acid (for example, manufacturing method currently indicated by the U.S. Pat. No. 2,758,987 item), The annular dimer of lactic acid and aliphatic hydroxycarboxylic acid, for example, lactide and glycolide, and epsilon-caprolactone, A ring-opening-polymerization method which polymerizes under existence of a catalyst (for example,

manufacturing method currently indicated by the U.S. Pat. No. 4,057,537 item), How to carry out dehydration polycondensation of the mixture of lactic acid, aliphatic series dihydric alcohol, and aliphatic dibasic acid directly. (For example, a manufacturing method currently indicated by U.S. Pat. No. 5,428,126), How to condense polylactic acid, aliphatic series dihydric alcohol, aliphatic dibasic acid, and polymer under organic solvent existence. Although it faces manufacturing a polyester polymer by performing a dehydrating polycondensation reaction for (for example, the manufacturing method currently indicated by the European patent gazette 0712880A No. 2) and lactic acid under existence of a catalyst and the method of performing solid state polymerization at least some processes etc. can be mentioned, The manufacturing method in particular is not limited. Aliphatic polyhydric alcohol like a small amount of glycerin, aliphatic series polybasic acid like butanetetracarboxylic acid, Polyhydric alcohol classes, such as polysaccharide, may be made to live together, and copolymerization may be carried out, and a molecular weight may be raised using binding materials (polymers chain elongation agent), such as a polyisocyanate compound.

[0010]The polylactic acid used by this invention has the melting point called for by the method of mentioning later the polylactic acid mentioned above especially in the resin used as the main ingredients.

[0011]In the method of manufacturing fizz particles by this invention, ** Use the resin which uses as the main ingredients the polylactic acid in which the melting point is shown as above-mentioned, ** When heating this resin more than the melting point, and carrying out melting and ** Ranking second and quenching this resin that carried out melting below to glass transition temperature make a resin particle, are important, Adjustment of the ambient temperature conditions at the time of impregnating with diacid-ized oxygen which is a foaming agent for giving foaming ability to ** resin particle, and the amount conditions of being foaming agent impregnated is important. In this invention, in order to manufacture fizz particles preferably, a resin particle is first made from base material resin. After it heats this resin particle beyond the temperature which this resin fuses enough and it carries out melt kneading of the base material resin with an extrusion machine, for example, After quenching by extruding to strand shape and sinking the extrusion thing of this strand shape, An amorphous state or the calorific value in the differential scanning calorimetry of a low crystallized state can obtain the thing of 15 or more J/g by cutting to proper length or quenching a strand suitably simultaneously with cutting after cutting to length. In addition, as a method of manufacturing a resin particle from base material resin, It can obtain also by extruding tabular or massive, after heating base material resin beyond the temperature which this resin fuses enough and carrying out melt kneading with an extrusion machine, crushing this cooling resin or fracturing in the shape of a lattice, after quenching this extrusion thing with a cooling press, a mist cooling system, etc. The weight per one of the resin particle obtained from base material resin

is preferably good to make [0.05-10-mg] it 1-4 mg. If this particle weight becomes smaller than said range, manufacture of the resin particle will become difficult. The shape in particular of this resin particle cannot be restrained, but can be various kinds of shape, such as a spherical shape and rod form besides being pillar-shaped (pellet type).

[0012]In order to obtain tabular base material resin and massive base material resin for obtaining a resin particle as mentioned above in this invention, or in order to extrude to strand shape and to obtain a resin particle, When cooling the resin which uses the polylactic acid in a molten state as the main ingredients and solidifying, the resin particle obtained by quenching performing the cooling as aforementioned is made into the thing of a low crystallized state or an amorphous state. the cooling rate in this case -- in general -- by 2000 **/, above, it is above by 3000 **/preferably, and although that upper limit in particular is not restrained, it is usually a 10000 ** part grade for /. The degree of crystallinity of the resin particle obtained is 10% or less still more preferably 20% or less preferably, and although the lower limit in particular is not restrained, it is usually about 0%. In this specification, the degree of crystallinity of a resin particle is called for from the ratio of the crystal peak area of a chart and peak gross area which were obtained by measuring using the X-ray diffraction device made from Physical science Electrician Business. In the DSC curve in a differential scanning calorimetry, the resin particle of the low crystallized state or amorphous state acquired by the above-mentioned rapid cooling treatment shows the exothermic peak of 15 or more J/g. Namely, the calorific value in a differential scanning calorimetry contains the crystalline polylactic acid in which the melting point is originally shown as the main ingredients, and, as for the resin particle of 15 or more J/g, points out the thing in a low crystallized state or an amorphous state by rapid cooling treatment. As for this calorific value of a resin particle, it is preferred that they are 15 - 50 J/g and also 20 - 45 J/g, and maximums are 80 J/g in general. This calorific value of this resin particle is the calorific value based on crystallization in 2 ** the temperature rise process for /of the polylactic acid of a low crystallized state or an amorphous state. It asks from the exothermic peak area of the DSC curve obtained when the calorific value in a differential scanning calorimetry is measured based on JIS K7122-1987 and temperature up of 1-4 mg of the resin particles is carried out to 200 ** with 2 ** the heating rate for /with a differential scanning calorimeter in this specification.

[0013]In the case of that in which base material resin has hygroscopicity, in the process which carries out melt kneading of the base material resin with an extrusion machine as above-mentioned, and is extruded to strand shape etc., it is preferred to dry base material resin beforehand. When the resin which held a lot of moisture is fed into an extruder, in a resin particle, When it is made to foam, and the air bubbles which have an adverse effect on the homogeneity of the air bubbles of a foamed particle mix or it carries out melt kneading with an extrusion machine, the physical-properties fall of base material resin takes place, and there is

a possibility that a melt flow rate (MFR) may become extremely large. In order to control degradation of resin, the method of using and carrying out vacuum suction of the extruder with a vent-port, and removing moisture from base material resin is also employable. Conditions are set up so that MFR of base material resin may not become extremely large about the upper limit temperature of said extrusion temperature conditions, either.

[0014]Said base material resin may add a color pigment or colors, such as black, gray, brown, blue, and green, for example, and may be colored. If the coloring resin particle obtained from colored base material resin is used, the foamed particle and Plastic solid which were colored can be acquired. As colorant, the paints of an organic system and an inorganic system, a color, etc. are mentioned. As such paints and a color, various kinds of publicly known things can be used conventionally. To base material resin, inorganic substances, such as talc, calcium carbonate, a borax, way acid zinc, and aluminium hydroxide, can be beforehand added as a cellular regulator, for example. When adding additive agents, such as a color pigment, a color, or an inorganic substance, to base material resin, an additive agent can be scoured to base material resin as it is, but it is preferred to usually make the masterbatch of an additive agent in consideration of dispersibility etc., and to knead it and base material resin. Although the addition of a color pigment or a color changes also with colors of coloring, it is usually preferred to consider it as 0.001 to 5 weight section to base-material-resin 100 weight section. The improved effect of expansion ratio can be acquired by adding an inorganic substance to base material resin. In this invention, mixing of additive agents, such as fire retardant, a spray for preventing static electricity, a weathering agent, and a thickener, is also possible.

[0015]If it assumes being discarded after a product's using it, high concentration addition of additive agents, such as paints and a cellular regulator, is not preferred. As for the obtained resin particle, it is preferred to save under the environment where the bottom of an elevated temperature and a high-humidity condition is avoided, and hydrolysis does not advance.

[0016]Next, the resin particle obtained as mentioned above is impregnated with carbon dioxide as a foaming agent, and it is considered as fizz particles at it. The method of impregnating a resin particle with carbon dioxide within a well-closed container, and obtaining fizz particles as a method of impregnating the resin particle in this case with carbon dioxide is preferably employable. As other methods, while making carrier fluid distribute a resin particle under existence of carbon dioxide in a well-closed container, it can stir carrying out the temperature control of the contents, and the method of impregnating with carbon dioxide in the particle etc. can also be used. Being impregnated of the carbon dioxide to a resin particle is carried out by usually pressing carbon dioxide fit in the well-closed container currently put into the resin particle, so that it may become a pressure range of 5 - 100 kgf/cm²G.

[0017]When impregnating a resin particle with carbon dioxide by this invention, the ambient

temperature (***) needs to fill a lower type. This ambient temperature is the temperature of the gas of resin particle atmosphere, when putting in a resin particle without carrier fluid and impregnating with carbon dioxide in a well-closed container, and when putting in a resin particle and impregnating with carbon dioxide with carrier fluid in a well-closed container, it is the temperature of this carrier fluid.

[Equation 3]

$$3 < \text{ambient temperature } [**] \leq -2.5X + 55 \quad (1)$$

X show the amount of being impregnated of the carbon dioxide to a resin particle [weight %] among said formula. There is a possibility that the problem of equipment when ambient temperature carries out industrial production in less than 3 ** may occur, and carbon dioxide impregnating equipment at low temperature, and fizz particle preservation equipment with last thing. When the fizz particles with which carbon dioxide was impregnated at this temperature are made to foam, it is difficult for the rate of a closed cell of the foamed particle obtained to fall, or for dispersion in apparent density gravity to become large, and for die shape reproducibility and the weld nature between foamed particles to obtain a good foamed particle. On the other hand, if ambient temperature exceeds (-2.5X+55), in high crystalline polylactic acid, it will become impossible to expect improvement in expansion ratio according to advance of extreme crystallization, and a foamed particle with low apparent density gravity will no longer be obtained. When it is going to carry out hot forming of the obtained foamed particle within a mold, there is a possibility that the dilatability of a foamed particle and the weld nature between foamed particles may fall, and a good foamed particle Plastic solid may not be acquired. As for especially (-3.0X+55) the ambient temperature at the time of impregnating with carbon dioxide to a resin particle, it is [below [*]] still (-2.7X+55) more preferred that it is below [**]. Especially in this invention, it is preferred that the amounts X of being impregnated of the carbon dioxide to said resin particle are 2.5 to 20 % of the weight and also 2.5 to 17 % of the weight. There is a possibility that you may not be made to fully foam to a resin particle when the amount of being impregnated is less than 2.5 % of the weight, and on the other hand, when the amount of being impregnated exceeds 20 % of the weight, there is a possibility that the dilatability and weld nature at the time of shaping in a mold of the obtained foamed particle may become insufficient. This is considered for crystallization of a resin particle to advance easily. Although the pressure of the carbon dioxide of the resin particle atmosphere in the carbon dioxide impregnation process to a resin particle changes also with the expansion ratio of the foamed particle made into the purpose, it is usually 5-100kgf/cm²G and impregnating time is for [10 minutes] - 24 hours.

[0018]In this specification, the amount of being impregnated of carbon dioxide (% of the weight) is calculated by a following formula.

[Equation 4]

二酸化炭素含浸量(重量%)=

樹脂粒子に含浸した二酸化炭素の重量(g) × 100

(2)

二酸化炭素含浸前の樹脂粒子の重量(g)+樹脂粒子に含浸した二酸化炭素の重量(g)

The weight of the carbon dioxide with which the resin particle in an upper type was impregnated is found from the weight differences of the resin particle before and behind being carbon dioxide impregnated, and the gravimetry of a resin particle decides that even 0.0001 g of that measures. Although based also on the amount of being carbon dioxide impregnated, the foamed particle obtained by this invention method is under the temperature conditions which crystallization about below ** does not follow in general (T_g^{**} -65), and can be preferably kept by saving under the pressure conditions of 5 - 100 kgf/cm²G in general. [0019]The fizz particles obtained by this invention are used as a raw material for foamed particle Plastic solids. What is necessary is to be filled up with this foamed particle in a mold, to heat it, and just to make it weld, after heating this fizz particle and considering it as a foamed particle, in order to consider it as a foamed particle Plastic solid using the fizz particles by this invention. The method to which carry out heat softening of the resin particle, and it is made to foam as a method to which fizz particles are made to foam can adopt preferably. That is, the fizz particles impregnated with carbon dioxide are heated, and this is made to foam. As a heating medium for making it foam, although a steam, air, nitrogen which carried out heating adjustment, etc. are mentioned, a steam is usually used. Although a publicly known method is conventionally employable as a method which heats fizz particles and to which they are made to foam, it is filled up with fizz particles and a steam is made to usually introduce and foam in a well-closed container. If the well-closed container is equipped with the puncturing valve to which an internal pressure is made to leak slightly, the air in a well-closed container can be eliminated and a foamed particle with uniform density will be easy to be obtained. the temperature, i.e., the foaming temperature, at the time of heating the resin particle impregnated with carbon dioxide -- usually - (glass-transition-temperature-30 **) (glass transition temperature of +60 **) of base material resin -- it is - (glass-transition-temperature-10 **) (glass transition temperature of +40 **) preferably. If foaming temperature is lower than said range, sufficient foaming will not take place easily, and if higher than said range, the problem that the foamed particle which the rate of a closed cell of a foamed particle falls, and shows a good moldability is hard to be obtained will occur.

[0020]As for a foamed particle obtained from fizz particles in this invention, it is preferred that apparent density gravity is 0.015 - 0.3 g/cm³, and it is still more preferred that it is 0.015 - 0.2 g/cm³. When density is larger than said range, there is fear of a physical-properties fall of a foamed particle Plastic solid which dispersion in density of a foamed particle becomes large easily, and the dilatability of a foamed particle in the hot-forming case and weld nature show

dispersion within a mold, and is acquired as a result. On the other hand, when this density is lower than said range, since expansion ratio is comparatively high, there is a possibility that molding shrinkage may serve as a big Plastic solid. It is preferred to save under an acquired foamed particle elevated temperature and conditions which avoid the bottom of a high-humidity condition and are not hydrolyzed.

[0021]In this specification, apparent density gravity of a foamed particle prepares a measuring cylinder containing 23 ** ethanol, 500 or more foamed particles (weight W1 of a foamed particle group) neglected on the 2nd on condition of 50% of relative humidity, 23 **, and 1atm are sunk into this measuring cylinder using a wire gauze etc., It asks by carrying out division process of the weight W1 (g) of a foamed particle group put into a measuring cylinder to the capacity V1 (cm^3) of a foamed particle group read from a part for an ethanol water level rise (W1/V1).

[0022]As for bulk density of a foamed particle obtained from fizz particles, it is preferred that it is 0.01 - 0.2 g/ cm^3 . In this specification, bulk density of a foamed particle prepares an empty measuring cylinder, To this measuring cylinder, 50% of relative humidity, 23 **, When 500 or more foamed particles (weight W2 of a foamed particle group) neglected on condition of 1atm on the 2nd are put in, it asks by carrying out division process of the weight W2 (g) of a foamed particle group put into a measuring cylinder to the capacity (bulk volume) V2 (cm^3) which a graduation of a measuring cylinder shows (W2/V2).

[0023]An average cell diameter of this foamed particle is 10-500 micrometers, and is 30-400 micrometers preferably. If this cell diameter is smaller than said range, since film strength is too weak at the time of hot forming, foam breaking etc. will arise, and it will become a bad Plastic solid of care-of-health recovery nature. Since film strength is too strong at the time of heat foaming when this cellular thickness is larger than said range, sufficient expansion will not arise but it will be the Plastic solid in which surface smoothness was inferior. In this specification, an average cell diameter of a foamed particle abbreviated-halves a foamed particle, asks for an overall diameter of all the air bubbles which exist in that foamed particle section, and about ten or more foamed particles, this operation is performed and it makes it an average cell diameter with an arithmetic mean value of this called-for overall diameter.

[0024]In order to manufacture a foamed particle Plastic solid, after being filled up with a foamed particle in a mold, it is preferred to fabricate by heating this foamed particle with heating media, such as steam and a hot wind. A foamed particle is mutually welded with this hot forming, and a united foaming object is given. As a mold for shaping in this case, a steel band belt currently used for a continuous molding device of a statement is used for a conventional metallic mold and JP,2000-15708,A. As a heating method, steam is usually used and the cooking temperature should just be a temperature which the foamed particle surface

fuses.

[0025]When manufacturing a foamed particle Plastic solid, it is preferred to give a gas beforehand to a foamed particle offered into a mold with inorganic gas, such as air, nitrogen, and carbon dioxide. Organic gas, such as butane, can also be used. By using a foamed particle which gave a gas as a foamed particle for shaping, fizz at the time of shaping of a foamed particle, a moldability, and recoverability improve. this gas -- desirable -- 0.3-4mol/(1000g foamed particle) -- it gives still more preferably within the limits of 0.7-4 mol/(1000g foamed particle).

[0026]In this specification, quantity of gas (mol/1000g foamed particle) of a foamed particle is calculated as follows.

[Equation 5]

気体量 (mol /1000g 発泡粒子) =

$$\frac{\text{気体増加量 (g)} \times 1000}{\text{気体の分子量 (g/mol)} \times \text{発泡粒子重量 (g)}} \quad (3)$$

The gas increase of stock (g) in said formula is calculated as follows. The weight 120 seconds after taking out 500 or more foamed particles to which internal pressure was raised, moving to the thermostatic chamber under the relative humidity of 50% and the atmospheric pressure of 23 ** within 60 seconds, putting on the balance in the thermostatic chamber and taking out this foamed particle is read by giving the gas with which a making machine is filled up. Weight at this time is set to Q (g). Next, this foamed particle is neglected for 240 hours in the thermostatic chamber under the relative humidity of 50%, and the atmospheric pressure of 23 **. In order that the gas of the high pressure in a foamed particle might penetrate a cellular film and might slip out of it outside with the passage of time, the weight of the foamed particle decreased in connection with it, and in 240 hours, since the balance is reached, the weight is substantially stable. The weight of this foamed particle 240 hours after the above is measured in the thermostatic chamber, and weight at this time is set to S (g). Any above-mentioned weight shall be read to 0.0001g. Let the difference of Q (g) and S (g) acquired by this measurement be a gas increase of stock (g) in (3) types. It is the method of making a foamed particle the method which is directly filled up with fizz particles in type, and carries out hot forming as other methods for acquiring a foamed particle Plastic solid, i.e., fizz particles, and not fabricating this foamed particle, but making fizz particles foam and weld within a mold, and making a foamed particle Plastic solid. This method makes the fizz particles of future a foamed particle, and there is a possibility that dispersion in the density of the Plastic solid acquired although excelled in the productivity of a Plastic solid as compared with the method of fabricating this foamed particle in a mold may occur.

[0027]Shape in particular of a foamed particle Plastic solid cannot be restrained, but the shape can be various kinds of shape, such as vessel shape, tabular, the shape of a barrel, a column,

a sheet shaped, and block like shape, for example. It excels in dimensional stability and surface smoothness. Density (g/cm^3) of a foamed particle Plastic solid is a thing of $0.01\text{-}0.2\text{ g}/[\text{cm}]^3$ preferably, and is called for by what is done for the division process of the Plastic solid weight WM (g) in volume VM (cm^3) calculated from an outside dimension of a Plastic solid (WM/VM).

[0028]In this invention, it is the melting point and glass transition temperature of base material resin. It measures based on JIS K 7121-1987. The melting point of base material resin is the temperature of the peak peak obtained from the 2nd DSC curve obtained by a differential scanning calorimetry. With the 2nd DSC curve obtained by a differential scanning calorimetry of said base material resin. With 10 ^{**} the heating rate for $/$, temperature up is carried out (here, a DSC curve obtained is called 1st DSC curve.), it ranks second to 200 ^{**} , with a differential scanning calorimeter, and $1\text{-}5\text{ mg}$ of base material resin is lowered to 0 ^{**} with 200 ^{**} to 10 ^{**} the temperature falling speed for $/$. Then, the 2nd DSC curve is said for a DSC curve again produced by carrying out temperature up to 200 ^{**} with 10 ^{**} the heating rate for $/$. When two or more temperature of the peak peak appears in this base material resin, let peak top temperature by the side of high temperature be the melting point most.

[0029]Let glass transition temperature of base material resin be the halfway point glass transition temperature of a point that a straight line which is in a longitudinal axis direction at the equal distance, and a curve of a step change portion of glass transition cross from a straight line which is obtained from the 2nd DSC curve obtained by a differential scanning calorimetry and which each baseline extended.

[0030]

[Example]Next, an example explains this invention still in detail.

[0031]After carrying out melt kneading of Examples 1-3, and 5, the comparative example 1 - 3 crystallinity polylactic acid (Lacty 9030 by Shimadzu Corp.), and the talc with an extrusion machine, It extruded to strand shape, after carrying out the quenching solidification of this strand above by temperature falling speed/of 3000 ^{**} by underwater [about 25 ^{**}] subsequently, it cut, and about 1.3 mm in diameter, about 1.9 mm in length, and about 3 mg [per piece] resin particle were obtained. Talc was added so that it might be set to 2000 ppm . Next, after adjusting the inside of the autoclave which has the content volume of 5L to the ambient temperature shown in Table 1, this resin particle 1000g was supplied. Carbon dioxide was pressed fit in autoclave via the pressure regulating valve, and the pressure in autoclave was adjusted to the pressure shown in Table 1, and was held for 15 hours. Next, the resin particle was taken out after extracting the carbon dioxide in autoclave. The amount of being carbon dioxide (carbon dioxide) impregnated of this resin particle is shown in Table 1. After being filled up with the resin particle impregnated with this carbon dioxide in the well-closed

container, it heated to the temperature which introduces a steam and is shown in Table 1, and the foamed particle which carried out expansion foaming was obtained. The apparent density gravity of this foamed particle, etc. are shown in Table 1. Although the rate of a closed cell of the foamed particle obtained in the above-mentioned example measured the rate of a closed cell 5 times respectively in each example, it was not less than 80% of thing altogether. Although dispersion in the apparent density gravity of a foamed particle was also small and measured apparent density gravity 5 times respectively in each example, all were settled within the limits of **5% of the apparent density gravity shown in Table 1. In this specification, the rate of a closed cell of a foamed particle is a value calculated using the foamed particle sample of bulk volume ³ of about 25 cm according to Procedure C of ASTM D-2856-70 [1976 Re-authorization]. It was filled up with the obtained foamed particle in the well-closed container, and pressurized with carbon dioxide, and after impregnating with the carbon dioxide shown in Table 2 to a foamed particle, a 200x250x10-mm metallic mold was filled up, and hot forming was carried out with the steam of the temperature shown in Table 2. The acquired Plastic solid recuperated itself at 30 ** for 24 hours. The density of the acquired foamed particle Plastic solid is shown in Table 2.

[0032]After carrying out melt kneading of example 4 crystallinity polylactic acid (Lacty 9030 by Shimadzu Corp.), and the talc with an extrusion machine, It extruded to strand shape, after carrying out the quenching solidification of this strand above by temperature falling speed/of 3000 ** by underwater [about 25 **] subsequently, it cut, and about 1.3 mm in diameter, about 1.9 mm in length, and about 3 mg [per piece] resin particle were obtained. Talc was added so that it might be set to 2000 ppm. Next, after adjusting the inside of the autoclave which has the content volume of 5L to the ambient temperature shown in Table 1, this resin particle 1000g was supplied. Carbon dioxide was pressed fit in autoclave via the pressure regulating valve, and the pressure in autoclave was adjusted to the pressure shown in Table 1, and was held for 15 hours. Next, the resin particle was taken out after extracting the carbon dioxide in autoclave. The amount of being carbon dioxide (carbon dioxide) impregnated of this resin particle is shown in Table 1. A 200x250x10-mm metallic mold was filled up with the obtained carbon dioxide impregnating fizz particles, and hot forming was carried out with the steam of the temperature shown in Table 2. The acquired Plastic solid recuperated itself at 30 ** for 24 hours. The density of the acquired foamed particle Plastic solid is shown in Table 2.

[0033]

[Table 1]

番号	基材樹脂		被覆粒子		CO ₂ 含浸条件		発泡条件		発泡粒子の性状	
	T _g (°C)	T _m (°C)	発熱量 J/g	温度 (°C)	圧力 (MPa)	CO ₂ 含浸量 (重量%)	発泡程度 (%)	被覆粒子 見掛け密度 (g/cm ³)	平均 気孔径 (μm)	
実施例 1	60	149	30	10	2	7.8	68	0.089	170	
実施例 2	60	149	30	10	2	7.8	80	0.040	280	
実施例 3	60	149	30	10	3	14.2	80	0.058	15	
実施例 4	60	149	30	10	3	14.2	—	—	—	
実施例 5	60	149	30	30	2	6.2	80	0.067	240	
比較例 1	60	149	30	40	3	6.2	96	0.190	110	
比較例 2	60	149	30	50	3	4.7	90	0.280	90	
比較例 3	60	149	30	50	3	4.7	80	0.840	80	

[0034]

[Table 2]

番号	付与した 気体	気体の 含浸量 (重量%)	気体の含浸量 (mol/1000g 発泡粒子)	成形温度 (°C)	成形体密度 (g/cm ³)	融着性	外観
実施例 1	CO ₂	5.6	1.3	114	0.087	○	○
実施例 2	CO ₂	8.7	2.2	114	0.050	○	○
実施例 3	CO ₂	11.3	2.9	120	0.063	○	○
実施例 4	—	—	—	120	0.068	○	○
実施例 5	CO ₂	8.1	2.0	120	0.057	○	○
比較例 1	CO ₂	2.6	0.6	114	測定不可	×	×
比較例 2	CO ₂	2.2	0.5	120	測定不可	×	×
比較例 3	CO ₂	0.4	0.1	120	測定不可	×	×

[0035]The following standards estimated the weld nature and appearance of the Plastic solid in Table 2.

(Weld nature)

O : the Plastic solid was made to bend and fracture, and when the Plastic solid fracture surface observed, material destruction of the foamed particle has been checked.

X: When trying to take out a Plastic solid from the inside of a metallic mold using pneumatic pressure, interfacial peeling happened in the surface of the foamed particles which constitute the Plastic solid, and the Plastic solid has collapsed.

(Appearance)

O : it excelled in surface smoothness and die shape reproducibility, and was good.

x: It was inferior to the weld nature between foamed particles, and where a metallic mold is opened, it has checked that much surface unevenness existed between foamed particles, so that a Plastic solid could not be picked out from a metallic mold.

The value of the ambient temperature at the time of being CO₂ impregnated [which was

shown in Table 1 by reference], the amount X of being CO₂ impregnated and -2.5X+55, or -2.7X+55 was shown in Table 3.

[0036]

[Table 3]

	CO ₂ 含浸量 : X (重量%)	雰囲気温度 (℃)	- 2.5X + 55 (℃)	- 2.7X + 55 (℃)
実施例 1	7.8	10	35.5	33.9
実施例 2	7.8	10	35.5	33.9
実施例 3	14.2	10	19.5	16.7
実施例 4	14.2	10	19.5	16.7
実施例 5	2.6	10	48.5	48.0
実施例 6	6.2	30	39.5	38.3
比較例 1	6.2	40	39.5	38.3
比較例 2	4.7	50	43.3	42.3
比較例 3	4.7	50	43.3	42.3

[0037]

[Effect of the Invention]According to the manufacturing method of this invention, the fizz particles excellent in the fizz which can obtain the foamed particle which gives the good polylactic acid foamed particle Plastic solid of die shape and foamed particle weld nature are obtained. The foamed particle obtained considering the fizz particles obtained in the process of this invention as a raw material has small dispersion in apparent density gravity, and its rate of a closed cell is also high.

The foamed particle Plastic solid acquired eventually is excellent in lightweight nature, dimensional stability, buffer nature, and a mechanical strength, and is suitably used as shock absorbing material, a packaging material, etc., and since it has biodegradability, the industrial meaning -- subsequent disposal becomes easy -- is great.

[Translation done.]